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(54) **Fiber glass prepared from low viscosity melted masses composed of metal oxides.**

(72) Invention of:

(33) (32) (31) Conventional Priority: **Patent application deposited in the United States of America, on December 11, 1970, No. 97.203 in the names of Lee Williams and Garland Elmo Scott, Jr.**

The present invention relates in general to glass fibers formed from metal oxide compositions and specifically, to glass fibers formed from metal oxide compositions whose viscosity at the liquidus temperature is below 100 poises, but above a minimal value of viscosity, which depends on the liquidus temperature.

Glass fibers are useful in many applications, in particular in the reinforcement of elastomer articles and in laminated composite structures. These fibers are in general characterized by a good combination of high resistance, rigidity and low density. However, high performance composite structures require in general high rigidity fibers such as those measured with the Young module. Compositions with high Young module in general tend to have low viscosity at the liquidus temperature, this last expression being defined as being a temperature for which the liquid phase and the crystalline phase exist in equilibrium. There is a certain number of related difficulties for preparing glass fibers from compositions having low viscosity at the liquidus temperature.

A principal difficulty in the drawing of very small diameter glass fibers from melted masses with low viscosity is the incapacity of the fiber to resist to the tensile force. When the tensile resistance of the material is exceeded, the fibrous current is fractured.

A second obstacle is the crystallization or devitrification. When the melted mass viscosity is approximately equal to 1,000 poises or more at the liquidus temperature, in general there is no difficulty to draw the glass fiber. For melted mass viscosity of about 100 poises, a certain devitrification occurs in the drawing of glass fibers and drawing interruption may occur. For viscosity of 10 poises or less, the production of glass fibers using classical drawing technique leads either to partially crystallized short fibers, or a complete interruption of the drawing process.

In classical drawing techniques, the melted mass is extruded through a large diameter orifice, 2,000 microns or more, and then drawn until obtaining the desired

diameter, in general about 25.4 microns or less, while cooling it. However, the devitrification is intimately linked, among other things, to the liquidus temperature at the maximal growth speed temperature of the crystals, and to the viscosity at the liquidus temperature or close to this temperature. The crystal growth speed in a metal oxide remained in its superfused is generally inversely proportional to the viscosity. So, the large dimension of the extruded mass in prior techniques limits the cooling speed, such that a fiber of a composition whose viscosity is low will crystallize before it can be hardened in its vitreous state.

As a consequence, a principal subject of the present invention is to foresee "essentially continued", "roughly vitreous" fibers from low viscosity metal oxide compositions at high liquidus temperatures. Essentially continued fibers are defined as fibers having at least an aspect ratio 1×10^3. A roughly vitreous fiber is a fiber having a crystallization degree below 10%.

The recent innovation of "film stabilization" techniques supplies fibers produced from melted masses having extremely low viscosity. Currents of materials having low viscosity tend to be decomposed into droplets a short time after their exit due to the superficial tension. It was found that the decomposition could be prevented by forming a solid film around the current. The film thus "stabilizes" the current in vitreous form during the solidification. A process according to which the stabilization is carried out consists of extruding the current in a gaseous atmosphere which has sufficient concentration and sufficient reactivity for forming a film around the current, the film being insoluble in the melted current and having sufficient resistance for preventing the rupture.

As it was previously indicated, the glass is formed when a liquid is superfused before it has the time for crystallizing. The formation of glass is favored when (1) the hardening times are short, (2) the ratio of nucleus formation is low, and (3) the crystal growth speed is low. In general, the hardening time and

the crystal growth speed were too high for forming vitreous fibers from several compositions. However, the applicant found that the use of stabilization technique allowed the formation of vitreous fibers. The small dimension of the exiting current allows one to have much shorter hardening times. In addition, the applicant noted and experimentally found that vitreous fibers could be prepared with film stabilization technique from melted masses having viscosity in a specified range. The compositions of melted masses were characterized as having less than 20% by weight of SiO_2, as being "essentially exempt of alkali", and they have viscosity at the liquidus temperature T_m which is:

1. lower than 100 poises, and
2. indicated with logarithm scale, higher than about

$$13 - \left[17{,}44 \left(\frac{T_m + 670{,}4}{T_m + 1670{,}4}\right)\right]$$

The expression "essentially exempt of alkali" is defined as being related to products having alkaline impurities present in quantity below 3% by weight.

The new points that are believed to be characteristic of the present invention are shown in the following claims. The present invention with other subjects and advantages could be better understood with reference made to the description, in relation with the attached drawings wherein:

The figure 1 is a transverse cross-sectional schematic view of an extruder with low viscosity.

The figure 2 is a graphic with semi-logarithmic scale indicating the range of viscosity (with poises on the y axis) wherein specified compositions form vitreous fibers with film stabilization process. The x axis carries the liquidus temperature in degree centigrade; and

The figure 3 is a comparison graphic of the characteristics of fibers formed from melted masses with film stabilization process and prior techniques in function of the melted mass viscosity. Letter A indicates the prior technique, B the vitreous fibers, C indicates the partially crystallized state, the viscosity being represented with poises at the scale placed at the drawing bottom.

As it can be seen in the figure 1, a set of crucibles 10 contains a low viscosity melted mass 11. The crucible 10 may be produced from an appropriate refractory material, such as the tungsten or the molybdenum, which is compatible with the operating temperatures of the melted mass 11. The orifice 12 placed in the lower part of the set of crucibles 10, communicates with a surrounded chamber 13 formed by the support 14. Inducing coils 15 surround a heating envelope 16 which, at its turn surrounds the set of crucibles 10.

During the operation, inducing coils 15 bring the pressurized material into the set of crucibles 10 to be melted. The melted mass is then extruded in the chamber 13 by the inert gas pressure located above the melted mass in the form of a free current 17.

The chamber 13 contains an atmosphere which, in presence of the melted current, forms a film around the current. The atmosphere may be of any gas which, in presence of the melted current, forms a film which is stable and insoluble in the melted current. However, it is preferably desirable to use an atmosphere, such as propane, which is decomposed in presence of the melted current, and forms a carbon film around the current preventing the interruption or rupture before the complete solidification occurs.

To form glass fibers, it was known longtime ago that the cooling speeds must be quite rapid to prevent the crystallization. It is also well known that the crystal growth speed is inversely proportional to the viscosity of the melted material. Thus, it is obvious that a melted current of material with low viscosity and large diameter has a great tendency to crystallize.

This fact may probably be better understood according to the relation:

(1) $$X = I\,\mu^3 t^4$$

wherein: X is the crystallinity degree lower than 10,

I is the isotherm ratio of the nuclei formation,

μ is the isotherm ratio of the crystal growth, and

t is the time at temperature T.

The time required for the hardening is measured from the liquidus temperature T_m to a

temperature T_g, for which the vitreous state is kinetically stable. The importance for the crystallization being produced is inferior to that which would be produced isothermally at the temperature T where $I\mu^3$ is a maximum. The temperature T is approximately 3/4 of the liquidus temperature and the superfused melted mass viscosity must be above 10^6 at the temperature T to prevent the crystallization. In using the modified equation called WLF equation (see William, M.L., Landel, R.F., and Ferry, J.D., Journal of American Chemical Society, 77 3701, 1955), the viscosity at the temperature T_m was calculated. The results are shown with the curve 20 in figure 2. The curve 20 corresponds to the equation:

$$(2) \quad \log_{\eta} = 13 - \left[17{,}44 \left(\frac{T_m + 670{,}4}{T_m + 1670{,}4} \right) \right]$$

wherein η is the viscosity in poises. Thus, for melted masses whose viscosity (in logarithmic units) is higher than those provided by the equation (2), the resulting fibers have a vitreous structure superior to 90%.

The prior technique is full of examples of vitreous fibers produced from compositions with high silica concentration, in particular superior to 20% by weight. The silica is well known for its aptitude for preventing the crystallization due to its high viscosity. In the case of metal oxides containing less than 20% by weight of silica, in particular for compositions containing high alumina concentration (superior to 50% by weight), the low viscosity has prevented until nowadays the formation of vitreous fibers. In extruding the fibers according to the described film stabilization technique, the applicant succeeded to produce great lengths of vitreous fibers. However, for the compositions whose viscosity at the liquidus temperature is lower than the one provided by the equation (2), the formed fibers will have less than 90% of vitreous aspect (see example 10). As the initial extrusion diameter of fibers is small in comparison to those formed with conventional techniques of extrusion, the cooling speeds are much higher (above 10^3 degrees per second). As it is possible to observe it with the vitreous state of the resulting fibers, the high cooling speeds provide more than to compensate the low viscosity of the melted material.

The figure 3 illustrates the range of the melted mass viscosity which allows the vitreous fibers to be extruded with techniques prior to the one found for the film crystallization. For a melted mass viscosity superior to about 100 poises at the liquidus temperature, the prior techniques not only had difficulties for preventing the interruption of the current but also supplied partially crystallized short fibers. However, the stabilization techniques extend the range of viscosity to a lower limit which depends on the liquidus temperature. In general the applicant found that this lower limit was lightly larger than about 2 poises.

The examples indicated below are the illustrations of melted materials which has been extruded in the form of vitreous fibers. The melted material viscosity was below 20 poises at the liquidus temperature. The melted materials have been extruded under inert gas pressure of about 2.8 to 4.2 kg/cm^2 through an orifice of approximately 25 to 254 micron diameter, placed at the bottom of a molybdenum crucible. The stabilizing gas was of propane at the ambient temperature and was under a pressure of about one atmosphere. The propane is decomposed by contact with a free melted current and formed a thin carbon film around the current. The proportions of the compositions indicated in the examples are expressed in percent by weight.

EXAMPLE 1

	Percents
Al_2O_3	60-75
CaO	25-40

EXAMPLE 2

Al_2O_3	50-70
CaO	20-47.7
SiO_2	1-10

EXAMPLE 3

Al_2O_3	60.9
CaO	26.4
MgO	3.6
SiO_2	9.1

EXAMPLE 4

	Percents
Al_2O_3	36-74
CaO	20-45
MgO	1-46.5

EXAMPLE 5

Al_2O_3	65
CaO	30
ZrO_2	5

EXAMPLE 6

Al_2O_3	55
CaO	10
MgO	10
SiO_2	17.5
ZrO_2	5
Li_2O	2.5

EXAMPLE 7

Al_2O_3	50-70
CaO	10-18.2
MgO	5-13.6
BeO	9.1-13

EXAMPLE 8

Al_2O_3	50-60
MgO	11-18
SiO_2	4-10
BeO	9.1-13

EXAMPLE 9

Al_2O_3	60
CaO	30
BaO	10

EXAMPLE 10

Al_2O_3	75-100
CaO	25-0

The composition viscosity at the liquidus temperature in the example 10 was below the one provided by the equation (2). The prepared fibers were crystalline, such those measured with diffraction of X-ray. So, this example shows that the compositions containing about 75% by weight of Al_2O_3 form crystalline fibers.

The fibers having the compositions of previous examples were measured and it was found that they had about 7.6 to 10.2 cm long. The crystallinity degree was below about 10%, such as the one indicated with x-ray diffraction. So, for the first time, within the limit of knowledge of the crystallinity that the applicant is informed, glass fibers having the aspect ratios above 1 or 2 x 10^3 for diameters of about 25,4 microns or more, have been produced from metal oxide compositions having low viscosity. Consequently, it is well understood that the changes of composition, for example, may be carried out by the persons who have experience in the technique.

The appreciation of certain aforementioned measuring values must take into consideration of the fact that they issue from the conversion of Anglo-Saxon units into metric units.

The present invention is not limited to the embodiments which are just described, on the contrary, it is susceptible to variations and modifications which will appear to the man of the art..

CLAIMS

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1. Vitreous and continued metal oxide fibers, having a concentration of SiO_2 not above 20% by weight, characterized by the fact that it has a viscosity at melted mass state below 100 poises at its liquidus temperature T_m and above the logarithmic value of:

$$13 - \left[17{,}44 \left(\frac{T_m + 670{,}4}{T_m + 1670{,}4}\right)\right]$$

2. Fiber according to claim 1, characterized by the fact that Al_2O_3 is present between 50 and 75% by weight, the complement being at least one of the compounds CaO, SiO_2, BeO, ZrO_2, Li_2O, or BaO.

3. Fiber according to claim 2, characterized by the fact that this fiber contains 60 to 75% by weight of Al_2O_3 and 25 to 40% by weight of CaO.

4. Fiber according to claim 2, characterized by the fact that this fiber contains 60.9 % by weight of Al_2O_3, 26.4% by weight of CaO, 3.6% by weight of MgO and 9.1% by weight of SiO_2.

5. Fiber according to claim 2, characterized by the fact that the fiber contains 55 % by weight of Al_2O_3, 10% by weight of CaO, 10% by weight of MgO, 17.5% by weight of SiO_2, 5% by weight of ZrO_2 and 2.5% by weight of Li_2O.

6. Fiber according to claim 2, characterized by the fact that the fiber contains 60 % by weight of Al_2O_3, 30% by weight of CaO, 10% by weight of BaO.

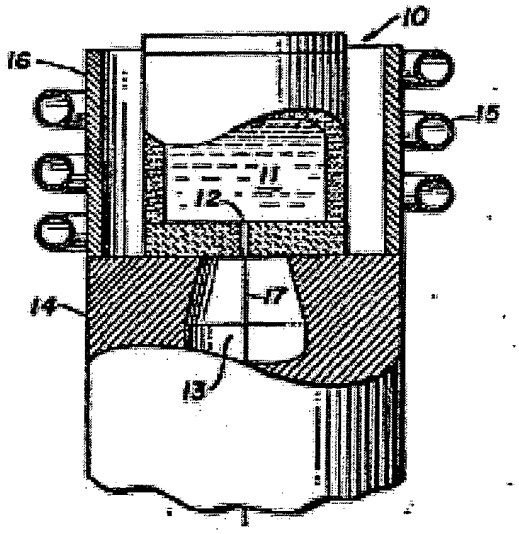

FIG. 1.

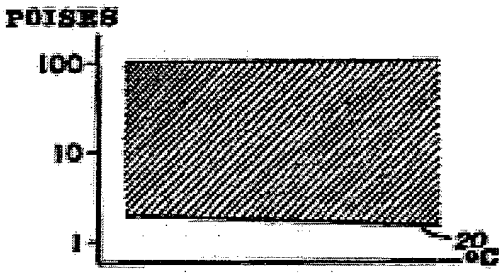

FIG. 2.

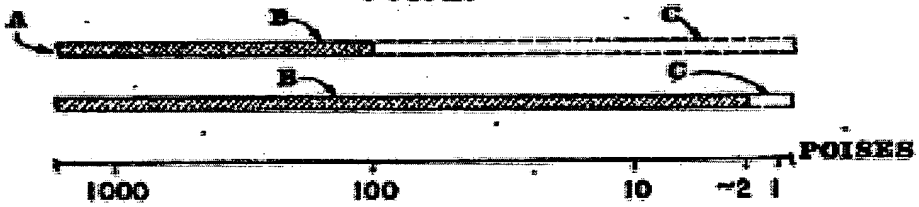

FIG. 3.

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